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Short communication

# Characteristics of flat-tubular ceramic supported segmented-in-series solid oxide fuel cell on all sides laminating using decalcomania method

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## HIGHLIGHTS

- SIS–SOFCs have been prepared using decalcomania method and tested.
- All sides laminating cell stack an OCV of 2.0 V and power output of 0.87 W at 800 °C.
- Excellent flat and uniform component layer using decalcomania method.

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## ABSTRACT

Solid oxide fuel cell components are fabricated using the decalcomania method. Then a flattened tubular segmented-series solid oxide fuel cell (SIS–SOFC) stack is prepared on each side (front, right, left and back sides) of ceramic support with a uniform thickness. SIS–SOFC laminated on all sides of the porous ceramic support show 2.6 times more active area per cell than the case involving only single side lamination. Power output increases by 2.5 times with higher open circuit voltage. This is attributed to the increase in active area per cell and sizable decrease in sheet resistance and polarization resistance by laminating the cells on all sides. For cells laminated on decalcomania paper, they show no sign of component materials penetrating through pores in ceramic support and have better interfacial bonding. Furthermore each cell component formed a uniform thickness layer.



## 1. Introduction

Solid oxide fuel cells (SOFCs) that operate at high temperatures have attracted much attention for the advantages they offer, such as high power, system efficiency, fuel flexibility, and low cost [1–5].

Segmented-in-series SOFC (SIS–SOFC), pioneered and demonstrated by Rolls-Royce [6], are currently being investigated. SIS–SOFC is fabricated using many cells connected in a series on an insulating porous ceramic support. Gas sealing, which is one of the problems for planar SOFC stacks, becomes easy in this configuration. In addition, high voltage and high power can be achieved by connecting SIS–SOFC stacks in series [7–9].

Currently, yttria stabilized zirconia (YSZ) for electrolyte support and NiO–YSZ for anode support are widely used for SOFC fabrication. For electrolyte support to reduce polarization and ohmic loss, however, the operation temperature should be ≥1000 °C. Furthermore, the anode support is 0.2–2 mm thick, which is much thicker than the anode layer of 5–500 μm thickness. Therefore, if complete sintering is not achieved, there will be sub-micron sized pores and higher oxygen loss during reduction of NiO. Since SIS–SOFC is not possible if component material is used as the support, partially stabilized zirconia (PSZ) with sufficient pores is widely used for long-term stability and fuel mobility.

To laminate SIC–SOFC, dip/spray coating [10,11] or screen-printing [8] using cell components containing slurry/paste is currently being used. As the slurry or paste is applied on porous support, the cell components penetrate through pores in the support. Consequently, the layer thickness may not be uniform and

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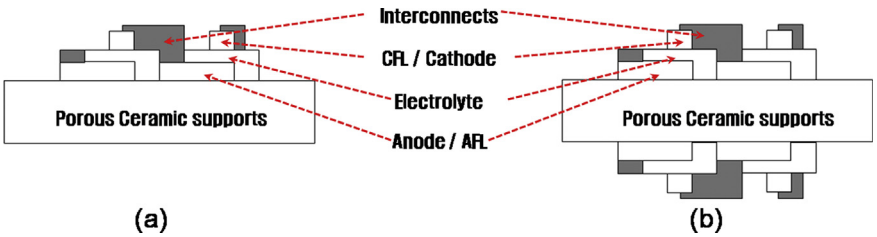


**Fig. 1.** Schematic diagram of SIS–SOFC cell stack (a) wet-slurry and (b) decalcomania paper.

crack or delamination can occur during sintering. Particularly, it is not possible to stack cells on every side for flat-tubular type cell.

Pillai et al. [8] reported that they fabricated SIS–SOFC using screen-printing method having active cell length of 1.3 mm on both sides of flattened tube. When they measured the current density, there was 5–10% difference from each side because the surface curvature of the support prevented cell component layer from having uniform thickness. Lai et al. [7] fabricated SIS–SOFC with active cell length of 0.4 mm on one side of the support. They found that the current density increased as sheet resistance and resistance loss decreased with increasing cathode thickness. There has been, however, no report on thin SIS–SOFC components laminated on all sides of porous ceramic support.

In this study SIS–SOFC is fabricated using decalcomania method in an attempt to demonstrate that it is a method to improve active area per cell [12,13] and efficiency of the cell. To achieve that, uniform layer of unit cell is prepared on all sides (front, back, right, left) of porous ceramic support. Then SIS–SOFC is fabricated by laminating each unit cell layer using decalcomania method. This study reports the analysis of bonding interface and electrochemical characteristics of SIS–SOFC fabricated by decalcomania method.

## 2. Experimental

NiO-YSZ (NiO supplied by Sumitomo Chem. Co, Japan and YSZ supplied by TZ8Y, Tosoh Co., Japan), YSZ, and $La_{0.8}Sr_{0.2}MnO_3$ (LSM, Fuel Cell Materials, USA) were used as anode, electrolyte and cathode, respectively. To build unit cell on decalcomania paper, pastes for each unit cell were prepared by mixing the starting material with decalcomania oil in the ratio of 1:0.5–0.7. The paste for each unit cell was then printed on decalcomania paper followed by room temperature drying for 24 h.

Flat-tubular supports are extruded using the YSZ plastic mass through a specially prepared die. A dry mixture for the support is made by mixing YSZ powder (Daejung, Korea), activated carbon as pore former and organic binders (YB131-D, YUKEN Industry, Japan).

The dry mixture is then mixed with water for several hours to prepare a dough and left to age overnight. The aged dough is extruded to form the flat-tubular support. The extruded supports are dried at 80 °C for 24 h and partially sintered at 1100 °C for 2 h in air.

To ensure uniform thickness, decalcomania transfer paper and solid layer are used separately when the unit cell is prepared. Anode/anode functional layer/electrolyte decalcomania paper is laminated on a pre-sintered porous ceramic support as shown in Fig. 1.

Afterward, it is sintered for 4 h at 1450 °C in air. Then cathode/cathode functional layer decalcomania paper is laminated and fired again for 2 h at 1250 °C in air to form SIS–SOFC.

The current–power–voltage performances of SIS–SOFC are investigated by measuring current and voltage at 750 °C and 800 °C using 3% humidified hydrogen gas as fuel and air as oxidant. For impedance measurement, SP-300 (Bio Logic, France) potentiostat is used in the range of 0.1 Hz–500 kHz. The microstructure and the interfacial reactions are studied with scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

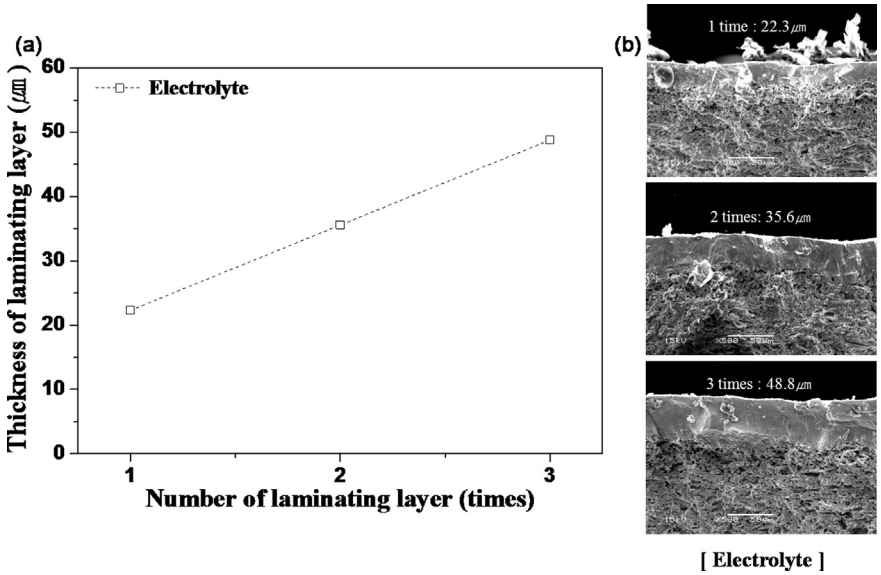


**Fig. 2.** a) A plot of layer thickness vs. number of layers. b) Cross-sectional SEM micrograph of the SIC–SOFC with varying number of layers (single to triple layers from top to bottom).

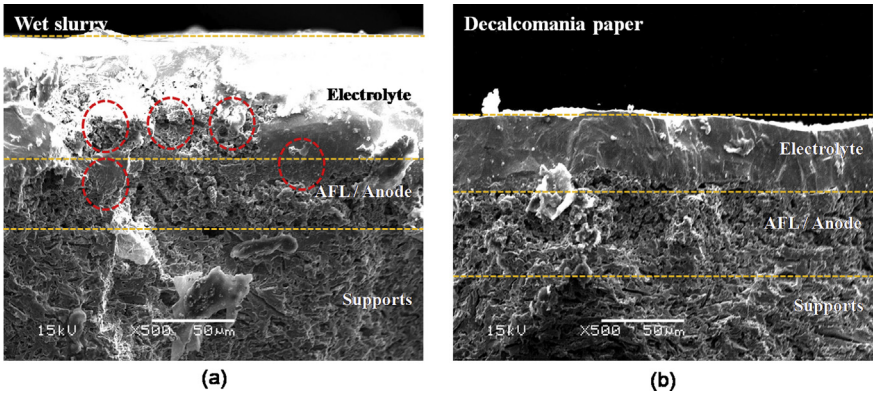


**Fig. 3.** Cross-sectional micrographs of electrolyte layers formed using (a) wet-slurry method and (b) decalcomania methods.

## 3. Results and discussion

Fig. 1 shows schematic diagram of SIS–SOFC on porous ceramic support with cells laminated on one side (a) and all sides (b). The active area of cell stack coated using slurry is 0.76 $cm^2$ when laminated on a single side and 2 $cm^2$ when laminated on all sides using decalcomania method. Consequently, it shows 2.6 times increase in active area per cell when laminated on all sides.

To verify whether the laminated layers form uniform thickness when laminated in decalcomania paper, samples with single, double and triple layers are prepared. Fig. 2(a) shows a plot of layer thickness vs. number of layers laminated. Fig. 2(b) shows cross-sectional view of the SIS–SOFC with varying number of layers (single to triple layers from top to bottom). The SEM micrograph in Fig. 2 shows the thickness increases linearly with increasing number of layers.

Fig. 3 shows microstructures of porous ceramic support/anode/electrolyte on decalcomania paper. Fig. 3(a) shows a layer fabricated with wet-slurry electrolyte, while Fig. 3(b) shows a layer fabricated using solid electrolyte. The circles in Fig 3(a) are pores in the electrolyte layer and slurry penetrated into anode functional layer (AFL)/anode layer.

When electrolyte is formed from slurry, it shows electrolyte penetrates through pores into the AFL/anode layer with no uniform electrolyte layer thickness. The electrolyte leakage causes defects and cracks in the electrolyte layer. It, in turn, causes decrease in efficiency of SOFC [14]. On the other hand, when solid electrolyte layer is formed on decalcomania paper, the layer is uniform and dense with no sign of penetration into the anode/AFL and better interfacial bonding as shown in Fig 4.

To study Ni/YSZ anode penetration into the porous PSZ support between slurry and decalcomania methods, cross-sectional areas are investigated with SEM/EDS as shown in Fig. 4. When the wet-slurry method was used to form anode layer, Ni/YSZ penetrates into the porous PSZ substrate. Consequently, the layer is not uniform as shown in Fig. 4(a). On the other hand, when the decalcomania method is used, it shows no interfacial penetration and forms uniform layer with good interfacial bonding as shown in Fig. 4(b).

Fig. 5 shows power output vs. current density of SIC–SOFC laminated on (a) single side and (b) all sides at 750 °C and 800 °C in humidified $H_2$ as fuel and air as oxidant. Open circuit voltage (OCV) and maximum power output show higher values for the cells laminated on all sides than the cells laminated on a single side.

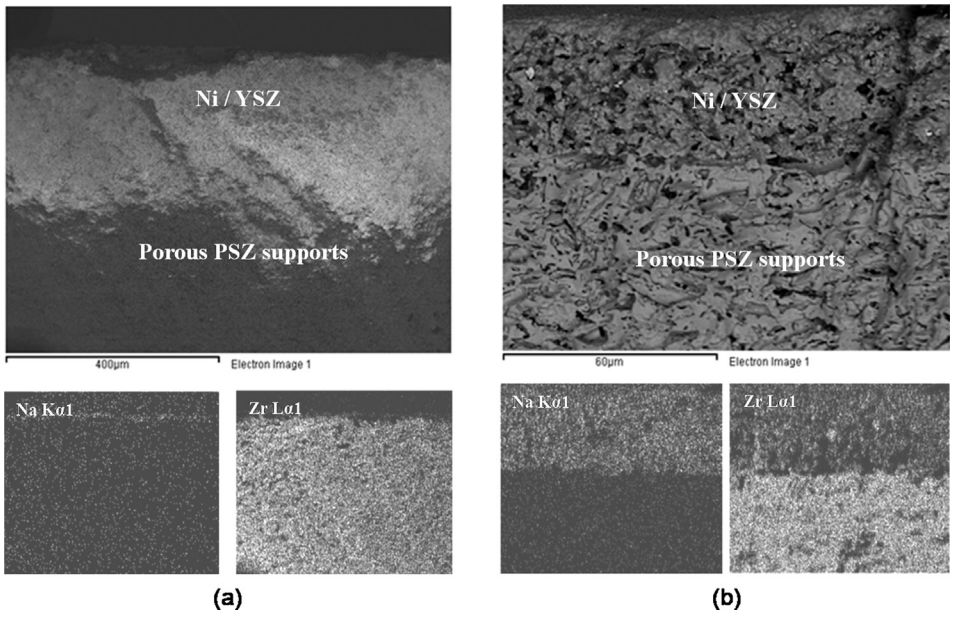


**Fig. 4.** Cross-sectional micrographs of anode layers formed using (a) wet-slurry method and (b) decalcomania methods.

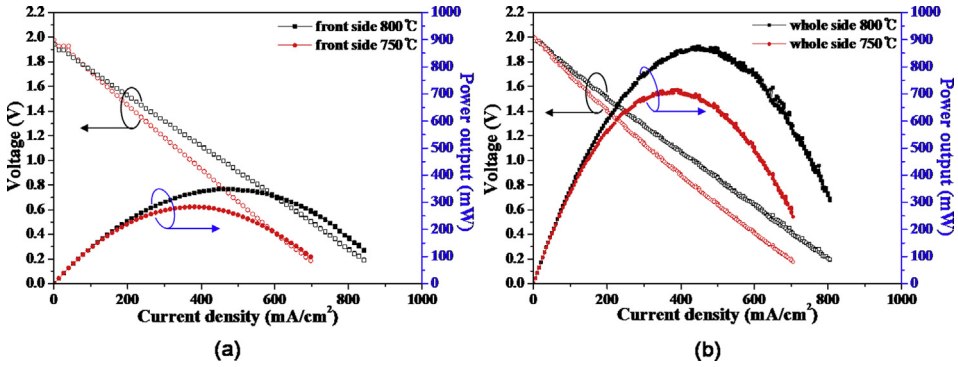


**Fig. 5.** Voltage and power output vs. current density curves of the SIS–SOFCs according to laminated area (a) one side and (b) whole side and with humidified $H_2$ as fuel and ambient air as oxidant from 750 to 800 °C.

At 800 °C, the OVC for SIC–SOFC laminated on single side is 1.98 V and 2.00 V when laminated on all sides. Pillai et al. [7] and Ni et al. [15] reported that the OVC for segmented-in-series modules at 800 °C was 0.91–0.96 V per cell. They attributed the observed OCV values which were lower than the theoretical value of ~1.1 V was due to leakage at the module end-seals and interconnects.

The reasons why this study shows better results than previously reported SIS–SOFC [7,8] and closer to the theoretical OVC value are as follows:

(1) The decalcomania method enables uniform and compact electrolyte layer.
(2) The compact electrolyte layer and better interfacial bonding prevents electrolyte penetrating into underlying layer.
(3) When laminated on all sides, matching shrinkage with unit cell creates less defects at the interfacial regions.

The power output at 800 °C is 349.2 mW for the single side lamination and 874.8 mW for all sides lamination. The active area increases by 2.6 times when laminated on all sides compared to lamination on single side. The measured power output as shown in Fig. 5 shows 2.5 times increase. This is attributed to increase in ohmic resistance at the interface since the more active area, the more contact area between anode and cathode.

Zhu et al. [16] reported that planar SOFC showed larger active area per cell as cathode area increases and that the internal resistance increases due to increased current path. When decalcomania method is used to fabricate SIS–SOFC, the current flows along the sides. The uniform conductor width on all sides reduces sheet resistance at the cathode. As a result, higher output can be achieved as shown in this study. This study also shows uniform power output on all sides, while SIC–SOFC fabricated with wet-slurry method shows 5–10% difference in power output between front and back sides [8].

The AC Impedance spectra at 750 and 800 °C for SIS–SOFCs with cells laminated on a single side (a) and all sides (b) are shown in Fig. 6. Since several cells are interconnected in series, the measured resistance in the figure is divided by the number of cells then multiplied by active area per cell. This is consistent with the methodology which Pillai et al. [7] used to calculate the impedance of SIS–SOFC. For impedance measured for cells laminated on all sides, high frequency horizontal axis intercept represents ohmic resistance and the arc in the low frequency represents polarization resistance. The ohmic resistance of cells laminated on all sides at 800 °C increased to 0.737 Ω cm$^2$ from 0.459 Ω cm$^2$ for cells laminated on a single side. This is attributed to the increased interfacial area as the active area per cell increases. On the other hand the polarization resistance decreases by 35% from 0.995 Ω cm$^2$ to 0.649 Ω cm$^2$ for cells laminated on all sides and a single side, respectively. This is because 1) the current movement path did not increase due to uniform electrode width and 2) the sheet resistance decreased due to increased active area per cell as the length of electrode increased. This is also due to the polarization resistance having larger effect on the loss of SIS–SOFC. This is consistent with the reports for planar and tubular cell stacks [17].

## 4. Conclusion

To form uniform thickness and increase active area per cell, flattened tubular SIS–SOFC is fabricated using decalcomania method. For cells laminated on decalcomania paper, anode did not penetrate through pores in the support. They show better interfacial bonding and each layer with uniform thickness. When the unit cell is laminated on all sides of SIS–SOFC on a porous ceramic

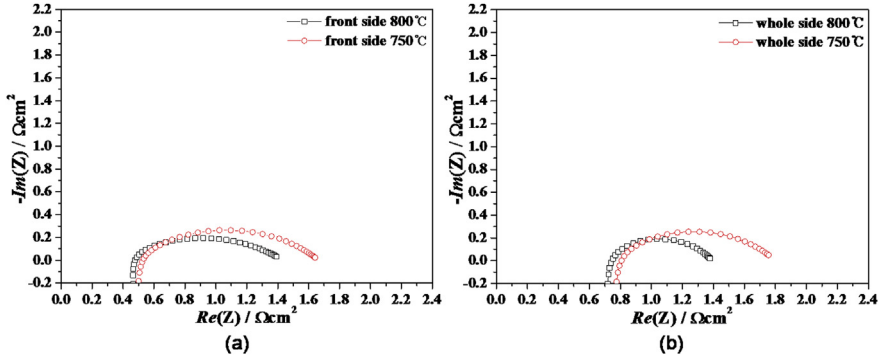


**Fig. 6.** AC Impedance spectra at 750 and 800 °C for SIS–SOFCs with cells laminated on a single side (a) and all sides (b). 3% humidified hydrogen gas as fuel at flow rate of (flow rate) and air as oxidant were used.

support, it shows 2.6 times more active area per cell than the case with a unit cell on a single side. The output increases by 2.5 times and the open circuit voltage also increases. This is because 1) the current movement path did not increase due to uniform electrode width and 2) the sheet resistance decreases due to increased active area per cell as the length of electrode increases. Impedance measurements show that the polarization resistance decreases by 35%. The reasons why this study shows better results are as follows:

(1) The decalcomania method enables uniform and compact electrolyte layer.
(2) The compact electrolyte layer and better interfacial bonding prevents electrolyte penetrating into underlying layer.
(3) When laminated on all sides, matching shrinkage with unit cell creates less defects at the interfacial regions.

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## References

[1] Y.T. An, B.H. Choi, M.J. Ji, K.J. Lee, H.J. Hwang, Solid State Ionics 207 (2012) 64–68.
[2] L. Besra, C. Compson, M. Liu, J. Am. Ceram. Soc. 89 (10) (2006) 3003–3009.
[3] R.K. Gupta, E.Y. Kim, Y.H. Kim, C.M. Whang, Met. Mater. Int. 15 (6) (2009) 1055–1060.
[4] I.J. Shon, S.L. Du, I.Y. Ko, J.M. Doh, J.K. Yoon, J.H. Park, Electron. Mater. Lett. 7 (2011) 133–137.
[5] M. Dokiya, Solid State Ionics 383 (2002) 152–153.
[6] F.J. Gardner, M.J. Day, N.P. Brandon, M.N. Pashley, M. Cassidy, J. Power Sources 86 (2000) 122–129.
[7] T.S. Lai, S.A. Barnett, J. Power Sources 164 (2007) 742–745.
[8] M.R. Pillai, D. Gostovic, I. Kim, S.A. Barnett, J. Power Sources 163 (2007) 960–965.
[9] K. Oh, J. Kim, S.H. Choi, D. Lee, J. Moon, Ceram. Int. 38 (2012) 695–700.
[10] T. Reitz, H. Xiao, J. Power Sources 161 (2006) 437–443.
[11] P.V. Dollen, S. Barnett, J. Am. Ceram. Soc. 88 (2005) 3361–3368.
[12] Y.T. An, M.J. Ji, S.M. Park, S.H. Shin, H.J. Hwang, B.H. Choi, Kor. J. Mater. Res. 23 (2013) 206–210.
[13] H.R. Cho, B.H. Choi, Y.T. An, S.H. Baeck, K.C. Roh, S.M. Park, Korean J. Met. Mater. 50 (2012) 685–690.
[14] K. Chen, X. Chen, Z. Lu, N. Ai, X. Huang, W. Su, Electrochem. Acta 53 (2008) 7825–7830.
[15] M. Ni, M.K. Leung, D.Y. Leung, Energy Convers. Manag. 48 (2007) 1525–1535.
[16] H. Zhu, R.J. Kee, J. Power Sources 169 (2007) 315–326.
[17] Y. Zhang, J. Liu, X. Huang, Z. Lu, W. Su, Int. J. Hydrogen Energy 33 (2008) 775–780.